1914

The determination of oils in limestone

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THE DETERMINATION OF OILS IN LIMESTONE.

BY

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A

THESIS

submitted to the faculty of the

SCHOOL OF MINES AND METALLURGY OF THE UNIVERSITY OF MISSOURI

in partial fulfillment of the work required for the

Degree Of

BACHELOR OF SCIENCE IN MINE ENGINEERING.

Rolla, Mo.

1914.

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INTRODUCTION.

The presence of organic matter in limestone has long been an established fact. In many deposits of metallic sulphides organic matter is thought to be very important as a precipitant of sulphides from sulphate solutions. In the Southeast Missouri Lead District, the occurrence of the ores is undoubtedly directly related to bands of chlorite and organic shale occuring in the limestone. It is also true in other districts that the deposition of sulphides is directly related to the presence of organic matter in the country rock.

In Wisconsin, and, to a larger extent, in northern England, shale oils have been manufactured on a commercial scale. These shale oils have a marked resemblance to petroleum.

The purpose of this work has been to establish the occurrence or the non-occurrence of petroleum in certain limestones. The results of this work, if oil were proved to exist, would have a direct bearing on the theories of the origin of oils.

PART 1.

THEORIES OF ORIGIN OF OILS.

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There are two principal theories of origin, The first, the inorganic or igneous theory; the second, the sedimentary or organic theory. The second is again divided into two more or less distinct parts,- one supposing the oils to be derived from the vegatable matter deposited with sediments; the other supposing the source to be the animal matter deposited with the shells which formed limestones. This work would support the animal organic theory if oil were proved to exist in the limestones.

The first theory postulates the formation of hydrocarbons by the action of water on metallic carbides in the regions of volcanic occurrence. There are many objections to this theory. While methane hydrocarbons have thus been formed in the laboratory by Moissan, Mendeléev and others, it is extremely doubtful whether large deposits are apt to be formed in the same way. The absence of volcanic activity contemporaneous with, or more recent than, the beds in which oil occurs, in even the remote neighborhood of oil deposits, acts strongly against the theory.

The sedimentary theories are much more generally accepted by geologists. These theories require the presence of vegetable or animal organic matter, or both, in beds of sedimentary rock. Destructive distillation of the organic matter is supposed to form hydrocarbons. The chief objection to the theory is the fact that under the same conditions in rocks having apparently the same characteristics, one bed contains oil while another does not. This is, however, not a very convincing argument.

There are strong arguments in favor of the theory; some of them follow. Oils occur only where there is a considerable thickness of sedimentary rocks below, and always occur in sedimentary rocks. It has been proved that hydrocarbons resembling the lighter portions of mineral oils can be manufactured from animal fat and vegetable matter. The aim of this work is to substantiate the sedimentary theory.

PART 2.

EXPERIMENTAL.

(a) Rocks Analyzed.

The limestones used in this work were from six horizons. Mr. H.A. Buehler, of the Missouri State Survey, donated three samples, and the rest were samples taken from localities near Rolla. The localities from which they were taken are given below.

Sample (1) was Cambrian Bonneterre dolomite, from the ore horizon in the Southeast Missouri Lead district; (2) Boone, Missipsipian limestone from quarries at Carthage, Missouri; (3) Plattin Ordovician limestone, from the southeast Missouri exposure of this bed; (4) Upper Gasconade limestone from the top of the Gasconade formation near Newburg; (5) Lower Gasconade, from the bottom of a zinc prospect shaft near Newburg; (6) Jefferson City pitted dolomite, Cambrian, from a quarry near Rolla.

The Bonneterre is a coarse, gray dolomite, containing some galena, marcasite, and secondary silica, with some rounded sand grains. The Boone is a fine white limestone, very pure, containing no appreciable amounts of silica or sulphides. The Plattin is a fine grained, dark, shaly limestone, with bands of calcareous shale.

Both the Gasconade dolomites are coarse, crystalline gray rock, with little silica and very little sulphide. The pitted Dolomite is a gray, porous rock, with some secondary silica, and possibly some small amount of marcasite. These rocks were all that were obtainable at the time that the work was started.

(b) Methods.

There were three methods employed in the analysis of the rocks, the first suggested by Mr. H.A. Buehler, and the other two by Mr. Mann and Professor Gottschalk.

The first method consisted of a solution scheme throughout. Two hundred samples of the limestones, through 40 mesh, were treated with a four percent solution of HCl. This strength was not maintained, but was approached by periodic additions of acid when the solution became neutral. (The amount of CO_2 gas evolved was sufficient indication of the strength of the solution.) This strength of solution has been used for soil analysis in determination of organic matter, and it was thought sufficiently weak to avoid breaking up any oils. A weaker solution required a very long time for the dissolving of the dolomites.

After the lime had been dissolved, (indicated by cessation of gas) the residue was filtered and washed in a gooch crucible, air dried, and powdered in a porcelain mortar. The powdered residue was then treated with petroleum ether, which was expected to dissolve out any mineral oils which might be present in the rocks. The mixture was allowed to stand for six hours, with frequent shakings, at the end of this time being placed in a funnel and the ether passed through a fine filter paper. The filtered ether was then allowed to evaporate, any residue from it being organic matter dissolved from the rock.

Method two was a distillation process. A small iron amalgam retort was used. The retort was three inches deep, two inches inside diameter at the top, one and one-quarter inches inside diameter at the bottom, holding about 150 grams of ground limestone. The cover, clamped by a screw clamp, fitted to the retort with a ground joint, insuring a perfect connection. The delivery tube was a one-quarter inch iron pipe, 18 inches long, attached to the cover by a screw connection. The delivery tube led into a water cooled Florence flask, connected by a tight cork stopper. The flask had a small arm with a pin point opening to the air, near the top of the neck. This was to prevent the expanded gas from breaking the flask or loosening

the connections when the retort was heated. The retort was heated by a gas blast burner.

The sample taken for this method was a 100 gram portion of the limestone, ground through 60 mesh. The limestones were heated at about 500° Centigrade for six hours. This temperature fluctuated from about 350° to 550° , but was as nearly as possible kept close to 500°.

Method three was a solution and distillation process. A 100 gram sample of limestone, through 60 mesh, was dissolved in a four percent solution of HCL, in the same way as in Method 1. The residue was dried and washed in the same way, and pulverized in a porcelain mortar. It was then placed in one of the retorts used in Method 2, and heated at about 500° Centigrade, for three hours. The volatilized material was , as in Method 2, caught in a water cooled Florence flask.

In none of these methods was the drying done by artificial heat, because water could not affect the work in any way, and heating might have caused the loss of some hydrocarbons.

CONCLUSIONS.

The results of this work are entirely negative. In no case whatever was any trace of oil found. The residue from the first method of treatment were dark colored when wet, but they became much lighter on drying. When the petroleum ether was filtered off and evaporated, nothing whatever was left in the beakers which had held the filtered ether. In the distillation scheme the only material condensed was water. In the third treatment an unmistakable odor of H_2S was noticed, from the Bonneterre sample. Some galena was present in the rock; it's presence is sufficie nt to explain the source of the H_2S.

It is possible that larger amounts of limestone would yield traces of oil. It requires, however, more and larger equipment than has been available for this work. The Distillation scheme is, apparently, the best and only rational method of working at the problem. The greater part of the time put on this work has been consumed in experimenting to find a method of prodedure.

The only conclusion that can be drawn is, that no oil which can be abstracted by the methods used, exists in the limestones analyzed. The work, therefore, has nogreat bearing on the theories of origin of oils. It cannot be

taken as positive proof of the non-existence of oil in limestones. A noteworthy fact is that only the Boone Mississippian limestone was taken from beds which are above Ordovician, and that no oil is known to exist in rocks below the Ordovician.

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